Elastic Measurements of Ferroelectrics for Probing the Piezoelectric Response and Structural Defects

F. Cordero[1*]
[1]CNR-ISC, Istituto dei Sistemi Complessi, Area della Ricerca di Roma–Tor Vergata,
Via del Fosso del Cavaliere 100, I-00133 Roma, Italy
*Francesco Cordero: francesco.cordero@isc.cnr.it

Elastic and anelastic measurements other than piezoelectric resonance are not included in the standard set of the techniques for characterizing ferroelectric (FE) materials. They are the elastic counterpart of the dielectric spectroscopy and therefore directly probe strain rather than electric polarization, both due to (anti)ferroelectric transitions and defects, and hence also the piezoelectric response. Being insensitive to the motion of the charge carriers, the elastic properties provide information especially valuable when a high conductivity dominates the dielectric response and hinders the piezoelectric one.

It is first shown that, under the usual conditions of anelastic spectroscopy, e.g. Dyamic Mechanical Analyzers at Hz, resonating bars at kHz or ultrasound measurements at MHz, in the FE phase there is a softening of electrostrictive and hence piezoelectric origin, which provides a measure of the piezoelectric response without need of poling the material. This feature should be useful when exploring new piezoelectric materials, not yet optimized with respect to defects, where the piezoelectric response is hindered by excessive conduction. What is generally recognized is the opposite effect of piezoelectric stiffening, namely the cancellation of the softening by the depolarization fields. We first present two particularly clear cases [Phys. Rev. B 93, 174111 (2016)]: *i)* PZT near the morphotropic phase boundary measured at frequencies of kHz, with fully developed piezoelectric softening, compared with Brillouin experiments, where within the short wavelength of the probing acoustic wave the depolarization field cancels the softening; *ii)* Zr-rich PZT where the softened FE phase is followed at lower temperature by a stiffer antiferroelectric (AFE) phase, compared with the same material doped with 2% La, where the FE phase transforms into incommensurate (IC) AFE and the steps in the stiffness disappear.

Aging and repeated cycles of anelastic measurements of the last two samples across the FE/AFE and IC-AFE/AFE phases provide another type of information [J. Appl. Phys. 120, 064104 (2016)], useful in evaluating the suitability of an AFE material to applications that exploit the FE/AFE transition, such as high displacement actuators or high energy storage capacitors. In fact, PZT with ~0.05 Ti exhibits rather slow kinetics of transformation from FE to AFE, with coexistence of the phases at room temperature. Upon thermal cycling and aging at room temperature the Young's modulus of PZT can become more than 4 times softer, but the original state can be recovered by , even quickly, at 400-600 ^{o}C. The defects responsible for this behavior are not yet identified, but likely are clusters of O vacancies at the walls between the FE and AFE domains, which are source of electric and stress fields. In fact, in La doped PZT, where the FE phase with large volume and depolarization fields is substituted by the IC-AFE phase, the elastic modulus remains unchanged within 0.3% over more cycles and longer aging than in the previous case.